

Relaxation of conductivity in amorphous multi-component chalcogenides of copper and silver

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Abstract. Amorphous materials in the system $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ ($0.6 \leq x \leq 1.0$) show polarization phenomena. The time dependences of the conductivity and the ionic component of the conductivity in the studied materials were investigated.

1. Introduction

Multicomponent copper and silver chalcogenides have been known as promising materials with the ionic conductivity by silver and copper ions. The electric properties of glassy materials $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ had been studied in the broad ranges of pressure, temperature and electric field frequency [1-3]. Studied materials are mixing (electron - ionic) semiconductors with a predominant share of the ionic component of the conductivity. This paper is devoted to studies of the relaxation processes in $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with x varying from 0.6 to 1.0.

2. Results and Discussion

The glassy materials $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ were obtained by quenching from the melt [2]. Glass surfaces were studied with scanning electron microscopes JEOL-JSM6390LA, Auriga CrossBeam Zeiss and microanalysis of samples was carried out using an energy-dispersive X-ray microanalyser on a fresh fracture of samples. These studies confirmed that all bulk glasses were homogeneous.

Studied materials have the ionic conductivity therefore it assumed that there the ion-relaxation polarization appears. For verifying this assumption, the relaxation time of carriers was estimated from analyzes of the frequency dependences of real and imaginary part of impedance (figure 1). The relaxation time of carriers is $\sim 6 \cdot 10^{-5}$ s. This time is typical for ion-relaxation polarization in amorphous materials, which is caused by the excess transfer of weakly bound ions under the effect of an electric field to distances on the scale of sizes that describe the structure.

The relaxation processes, connected with the migration polarization, in amorphous $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ were investigated by means of DC measurements in the cells with blocking and semi-reversible electrodes relative to ion component of the conductivity. Studied materials have a mixed electronic and ionic conductivity, the ionic component of conductivity varying from 72 to 99 percent depending on the concentration of silver and copper. At the first moment, when a constant voltage is applied to samples, the samples show the total (electronic and ionic) conductivity, and then the conductivity decreases until the constant level (electronic conductivity) (figure 2a, 2b). It is due to



a gradual reduction of the ionic component of the conductivity in connection with the polarization phenomena, which is due to formation at the boundary sample - electrode double electric layer.

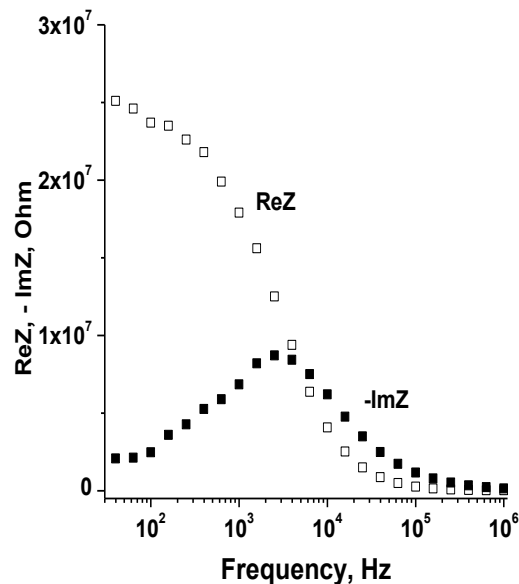


Figure 1. The frequency dependence of real and imaginary part of impedance of $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x=0.6$. The measurements were obtained using Solartron 1260A at room temperature under atmospheric pressure.

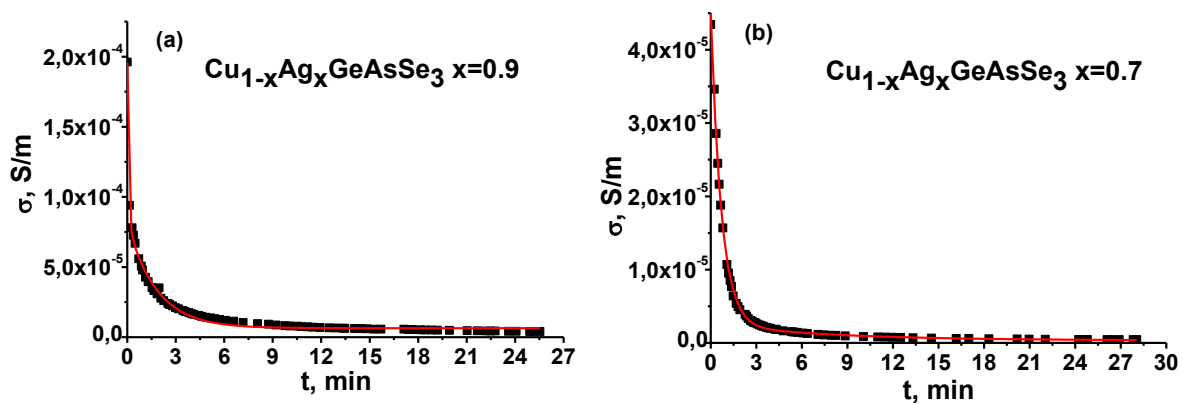


Figure 2. (a) – The time dependence of conductivity $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x=0.9$. (b) – The time dependence of conductivity $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x=0.7$. The measurements were obtained using Solartron ModuLad at room temperature under atmospheric pressure using semi-reversible copper electrodes with the graphite filter.

The time dependence of conductivity of the amorphous $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ is best approximated by the exponential function as in the equation (1).

$$\sigma_i = a + b \cdot e^{\frac{t}{t_1}} + c \cdot e^{\frac{t}{t_2}} \quad (1)$$

It can be assumed, that the times t_1 and t_2 characterize the relaxation processes in the amorphous $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$. One time (t_1) is always bigger than the other (t_2). One can assume, that the first, smaller time (t_1) characterizes the relaxation process at the boundary sample - electrode; the other, bigger time (t_2) characterizes the relaxation process related with the diffusion flow of ions, which is probably determined including by the atomic structure of the amorphous $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ [4]. Also, at single exponential approximation, an average relaxation time has been obtained. This average time (t) is closely to the time t_1 . It means that the main contribution to the conductivity relaxation is introduced by the processes at the boundary sample – electrode.

These times t_1 and t_2 vary depending on the electrode. When the conductivity time dependences were measured using blocking graphite electrodes these times generally appeared bigger then when measurement were carried out using semi-reversible copper electrodes with the graphite filter on cathode (table 1). It can be assumed, that this fact confirms appearance of ionic conductivity by copper ions and also it confirms the assumption that the main contribution to the conductivity relaxation is introduced by the processes at the boundary sample – electrode.

Table 1. Comparison of the relaxation time in measurements using copper electrodes with the graphite filter on cathode and using graphite electrodes.

x	Copper electrodes with the graphite filter on cathode			Graphite electrodes		
	t_1 , sec	t_2 , sec	t , sec	t_1 , sec	t_2 , sec	t , sec
0,95	11,60465	201,7216	13,6002	39,5662	597,188	44,5444
0,9	4,59127	108,7045	42,00854	36,6004	411,6132	169,8272
0,85	33,26861	311,9522	166,58	161,8194	1350,912	496,0305

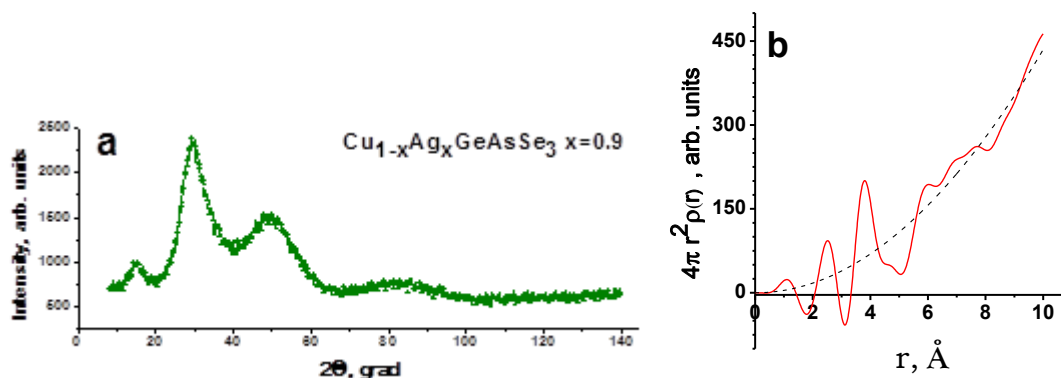


Figure 3. (a) - Powder diffraction patterns of compounds $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x = 0.9$. (b) – The experimental radial distribution function of amorphous atoms $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x = 0.9$.

For verifying the assumption that the relaxation processes in amorphous $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ is connected with their structure, the detail structure analyzes of studied materials is necessary. X-ray qualification of materials (figure 3a) has been performed with diffractometer Shimadzu XRD 7000 (monochromatic radiation $\text{CuK}\alpha$). The experimental radial distribution function RDF of $\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$ with $x = 0.9$ (figure 3b) was obtained from the X-ray analysis data. The initial analysis of experimental RDF was carried out in ideas of the fragmentary model [5, 6]. This analysis showed that studied materials have layered structure. This layers is formed by randomly alternating tetrahedrally coordinated atoms of germanium and silver via selenium and arsenic atoms [4]. It should be mentioned that the part of the silver atoms are not included in described structure units, and it can easily move between layers. This conception of studied materials structure is verified by the analysis of the structure using the Raman scattering methods. The Raman scattering was obtained using Probe NanoLaboratory NTEGRA Spectra (NT-MDT, Russia), which comprises high resolution confocal

scanning laser microscope, Raman spectrometer, and scanning probe microscope (SPM). The Raman scattering of stone chip of amorphous AgGeAsSe_3 ($\text{Cu}_{1-x}\text{Ag}_x\text{GeAsSe}_3$, $x=1$) is presented on figure 4. Since investigated materials are multicomponent and it is very difficult to analyze all possible bonds, only the most basic reflexes will be considered. There are two intensity maxima at 140 cm^{-1} and 193 cm^{-1} , which may correspond to vibrations of Ge-As and Ge-Se (tetrahedra with four-coordinated germanium atom in the centre) bonds, respectively [7]. Also there are two small maxima at 210 cm^{-1} and 240 cm^{-1} , which may correspond to vibration of As-Se ($\text{AsSe}_{3/2}$ pyramids) and Se-Se bonds, respectively [7].

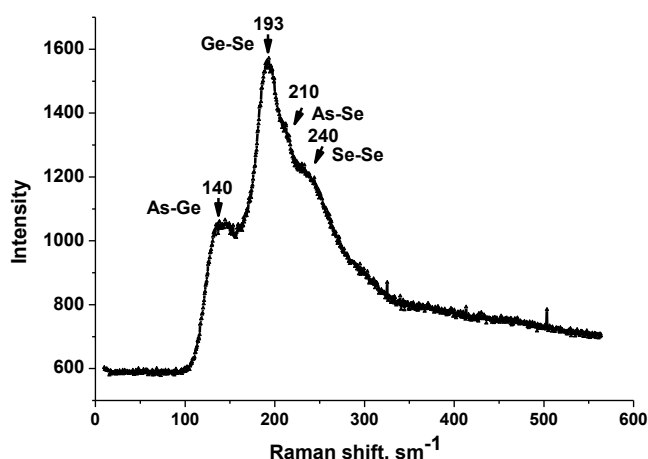


Figure 4. Raman spectra of AgGeAsSe_3 . The He-Ne laser with $\lambda = 633\text{ nm}$ and power 30 mW was used as a pumping source.

3. Conclusion

The time dependences of conductivity were analyzed. It can be approximated by exponential functions, and exponential indices characterize relaxation processes in studied materials. Relaxation processes are determined by atomic structure and processes at the boundary sample – electrode. And the main contribution to the conductivity relaxation is introduced by the processes at the boundary sample – electrode.

Acknowledgments

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References

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